Temporal and Spatial Natural Variability of the $\delta^{13}C$ of Dissolved Inorganic Carbon in Seawater

A Senior Thesis

Submitted as Partial Fulfillment of the Requirements

For the degree Bachelor of Science in

School of Earth Sciences at

The Ohio State University

By

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The Ohio State University, Spring Quarter 2007

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This manuscript is written for submission to the journal Global Biogeochemical Cycles.

ABSTRACT The natural variability of the $\delta^{13}C$ of dissolved inorganic carbon (DI-$\delta^{13}C$) in seawater at temporal and spatial scales is poorly documented except for at a handful of long-term monitoring sites. The lack of such data limits our ability to understand the regional natural variability in DI-$\delta^{13}C$ and oceanic uptake of atmospheric CO_2. Seawater DI-$\delta^{13}C$ was measured in Hawaii, Gulf of Panama, Palau, and Saipan at ~weekly resolution for a period of up to three years. We found that in Panama, DI-$\delta^{13}C$ varied seasonally with upwelling. During upwelling, deep, cool, nutrient-rich, and isotopically depleted DIC waters are brought to the surface. In Palau and Saipan, the DI-$\delta^{13}C$ increased steadily from 2001 to 2003 with no evidence of seasonal variation. These results suggest that DI-$\delta^{13}C$ in the western tropical Pacific is likely controlled by processes that occur on larger scales such as changes in currents and/or water mass movements. In Hawai'i the lack of a relationship between temperature, chlorophyll, and DI-$\delta^{13}C$ indicate that land and coastal interactions may influence DI-$\delta^{13}C$. The variability in DI-$\delta^{13}C$ values at Palau, Saipan, and Panama appear to be controlled by open ocean processes whereas the Hawai'i values appear to be influenced primarily by coastal processes.

INTRODUCTION

DI-$\delta^{13}C$ Natural Variability

Open ocean DI-$\delta^{13}C$ in seawater is controlled by three main factors. These factors are: 1) physical processes such as advection, mixing and ocean-atmosphere gas interactions, 2) chemical processes such as alkalinity and CO_2 solubility, and 3) biological processes such as respiration and photosynthesis(Quay, Stutsman 2003). In coastal environments, the contribution of terrestrial carbon to the coastal ocean carbon cycle can be the most significant factor (Bauer et al. 2001). Over time, the variation in DI-$\delta^{13}C$ values at any given site can vary due to changes in the proportionate contribution of each factor.

Physical processes that take place in the overlying atmosphere and within the ocean contribute to the overall DI-$\delta^{13}C$ values in seawater. Ocean currents play a significant role in moving seawater masses in the ocean causing mixing and replacement in the water column. Horizontal advection can bring surface water masses into an area causing a change in DI-$\delta^{13}C$, sea surface temperature, and nutrient abundance. The deep water masses are normally cool, nutrient rich and DI-$\delta^{13}C$ depleted due to the respiration and decay of organic material as it sinks to the bottom [(Lin et al. 1999; Peeters et al. 2002)]. Air-water gas interactions can also affect the value of DI-$\delta^{13}C$ in seawater [(Wanninkhof 1992; Zhang et al. 1995; Gruber, Keeling 2001)].

Chemical processes contribute to the fluctuations in DI-$\delta^{13}C$ such as alkalinity and CO_2 solubility. An increase in the alkalinity of ocean water results in a greater amount of atmospheric CO_2 sequestration (Keeling et al. 2004) depletion DI-$\delta^{13}C$ values. Therefore water masses with greater DIC concentrations are unable to take up as much CO_2 as would water masses having lower DIC concentrations. The CO_2 solubility in the ocean is evaluated using many factors. The depth of the thermocline determines the ratio of cold and warm waters in the ocean which is stated to set the mean solubility constant of CO_2 in seawater (Ito, Follows 2003). Another factor that affects the solubility of CO_2 in the ocean is the surface residence time of water. The rate at which water is cycled at the sea surface is loosely related to the amount of atmospheric CO_2 that the ocean can sequester. The pressure gradient in the ocean can also contribute to the solubility of CO_2 (Teng et al. 1996). The fluctuating pressure gradients throughout the ocean can direct and detour the dilution of CO_2 in water masses. All of the

aforementioned factors controlling solubility in CO_2 are also able to fractionate the $\delta^{13}C$ value. Lighter carbon isotopes are preferentially diffused during equilibration of water masses with differing physical properties.

Biological activities are a major contributor to the fluctuations in DI-$\delta^{13}C$ values of seawater. Photosynthesis in the photic layer of the ocean contributes to the fractionation of DI-$\delta^{13}C$ (Erez et al. 1998). Photosynthetic organisms take up larger amounts of ^{12}C relative to ^{13}C due to differences in molecular weight which decreases the activation energy needed for carbon fixation during the Calvin Cycle (Popp et al. 1998). Respiration of organic material causes decreases in the DI-$\delta^{13}C$ of seawater (Zeebe et al. 1999a). The isotopically light carbon in the organisms remineralize as they sink and export the carbon back into the system as DIC (Takahashi et al. 2000).

Anthropogenic Factors on DI-$\delta^{13}C$

People and their actions are also able to cause fluctuations in seawater DI-$\delta^{13}C$. The burning of fossil fuels causes depletion of $\delta^{13}C$ in atmospheric CO_2, known as the Suess effect (Sonnerup et al. 2000). The atmospheric CO2 then invades the oceanic sink and drives down the DI-$\delta^{13}C$ value of the seawater [(Zeebe et al. 1999b; Quay et al. 2003; Keeling et al. 2004; Quay et al. 2007)].

Goals

The goal of my research was to explore the natural variability in seawater DI-$\delta^{13}C$ at four sites over the course of three years (Fig 1). Each site is geographically and oceanographically unique, thus providing a range of environments for monitoring seawater DI-$\delta^{13}C$. The Panama site is coastal, well-flushed, and experiences seasonal upwelling. The Palau site is located 2km from shore and is flushed by open water conditions. The Saipan site is coastal, but is also heavily flushed by open ocean conditions. The Hawaii site is coastal, in a protected bay that is not well-flushed, and is influenced by coastal runoff.

MATERIALS AND METHODS

Four sites were selected in the tropical-subtropical Northern Pacific Ocean. These sites are Panama, Palau, Saipan and Hawaii; representing three diverse regions within the Pacific Ocean (Fig. 1). Samples were collected in the Gulf of Panama off the coast of Isla Contadora (8.6°N, 79°W) from the dates beginning on the 9th of February 2003 to the 11th of July 2003 about every three days. The seawater in this area is strongly affected by intense seasonal upwelling events. The collection site in Palau is about 2 km off the Eastern coast of the island in an area called Short Drop Off (7°16.4'N, 134°31'E). The site was sampled at weekly intervals from the 26th of October 2001 to the 21st of July 2003. Palau is located inside the Western Pacific Warm Pool (WPWP), and the Intertropical Convergence Zone (ITCZ) is to the North of the island during Northern Hemisphere summers and to the South of the island during Southern Hemisphere summers. The collection site in Saipan is on the Northeastern coast in an area called The Grotto (15°12'N, 145°53'E). Samples were taken at about weekly intervals from the 8th of October to the 13th of June 2004. Saipan is north of Palau and located outside of the WPWP. The proximity of Palau and Saipan are taken into account when determining the spatial

limitations concerning regional DI-$\delta^{13}C$ trends. The sampling site for Hawai'i is located off Coconut Island in Kaneohe Bay (21°26.18'N, 157°47.56'W) which is on the Northeast side of the larger island of O'ahu. Samples were collected at about weekly intervals between the 1st of March 2003 and the 18th of May 2004. Hawai'i is located on the southern edge of the North Pacific Gyre.

Seawater collection and preparation

The method for collection of seawater and preparation for DI-$\delta^{13}C$ analysis was modeled after (Raymond et al. 2004) and (Quay, Stutsman 2003). The seawater was collected in pre-cleaned (bathed in 10% HCl for at least 24 hours and rinsed with nanopure water) polycarbonate bottles. The seawater was then filtered through a 2.0 μm quartz fiber syringe filter to remove any particulate matter into a needle vented 25 ml glass vial (pre-cleaned by 10% HCl bath for at least 24 hours, nanopure water rinse and baked at 550°C for two hours) containing 100 μl of saturated mercuric chloride to inhibit organism respiration. The vial was filled with about 25 ml of seawater to minimize the air-water equilibrium reaction and vented to accommodate atmospheric pressure. The vials were then kept in cool, dark conditions until time of preparation. Duplicate vials were produced most days to ensure accuracy of measurements.

Upon preparation, about 5 ml of seawater was drawn out of the vial with a syringe to give head space for vacuum line acidification. The remaining seawater was then acidified with one-half ml of 85% orthophosphoric acid under helium flow for 20 minutes to convert all DIC into CO_2. The resulting CO_2 was cryogenically isolated in a liquid nitrogen cold trap in a vacuum extraction line from other volatile gasses and then flame sealed in glass ampoules. A reference sample was processed every 10th extraction to ensure procedural competency.

Isotopic analysis

The $\delta^{13}C$ of the CO_2 was then measured using a Delta IV stable isotope ratio mass spectrometer coupled to a multiport inlet system. All $\delta^{13}C$ values were reported relative to V-PDB [$\delta^{13}C$= per mil deviation of ^{13}C:^{12}C (R) relative to the Vienna Pee Dee Belemnite limestone standard].

$$\delta^{13}C = (R_{SAMPLE} / R_{STANDARD} - 1) * 1000$$

The average standard deviation for the measured $\delta^{13}C$ was ± 0.099‰ based on the duplicate samples taken (n=47).

Seawater Temperature

Temperature loggers were placed at each sampling site in the water at approximately the same depth that the DIC samples were taken. The temperature loggers recorded the sea surface temperature (SST) in degree Celsius every hour during the same time frame that the DIC seawater samples were taken. The hourly temperature recordings were averaged into a daily SST and then used to compare to the DI-$\delta^{13}C$.

Chlorophyll a

The Chlorophyll *a* data used in this study were acquired using the GES-DISC Interactive Online Visualization and Analysis Infrastructure (Giovanni) as part of the NASA's Goddard Earth Sciences (GES) Data and Information Services Center (DISC). The spatial resolution of the satellite imagery is 9 km x 9 km and temporal resolution is an averaged monthly value of milligrams per cubic meter. Measures were taken so as to not incorporate any terrigenous Chlorophyll *a* activity.

RESULTS

The data shows variations in seawater DI-$\delta^{13}C$ values over time (-1.108‰ to 1.571‰), among locations (Panama 1.014 ±0.335‰, Palau 0.675 ±0.280‰, Saipan 0.337 ±0.703‰, and Hawai'i 0.269 ±0.318‰), and over time within each location (Fig 2). These data confirm previous findings (Quay, Stutsman 2003) that different ocean-atmosphere-coastal processes are occurring simultaneously in different regions of the Pacific Ocean.

Panama DI-$\delta^{13}C$

The DI-$\delta^{13}C$ value in Panama increased from February to May fluctuating drastically and then decreased from May to July with less drastic fluctuations (Fig. 3). DI-$\delta^{13}C$ decreased in relation to upwelling event pulses. The intensity of DI-$\delta^{13}C$ depletion is related to the intensity of the SST decreases during upwelling pulses. The DI-$\delta^{13}C$ decreases post upwelling on an average of 0.26‰ $month^{-1}$ from 1.44‰ to 0.78‰. During the upwelling event, six major upwelling pulses were observed with minimum temperatures of 22°C, 21°C, 22°C, 24°C, 23°C and 25°C, respectively, frequencies occurring as little as a week and as long as a month between pulses. On average, the temperature increased during the upwelling event. After the upwelling event ceases, the SST steadies to about 28.5°C. Chlorophyll *a* concentration decreased over the given upwelling period starting at a value of 2.52 mg m^{-3} and ending with 0.75 mg m^{-3}. The Chlorophyll *a* concentration leveled off at ~0.6 mg m^{-3} after the upwelling event ceased. The DI-$\delta^{13}C$, SST and chlorophyll *a* were coupled during upwelling (February to May). Afterwards, the DI-$\delta^{13}C$ lightened independent of the coupled SST and Chlorophyll *a* after upwelling ceased (May to July).

Palau DI-$\delta^{13}C$

The DI-$\delta^{13}C$ value gradually increased over the entire record fluctuating from October 2001 to October 2002 followed by a steady increase throughout the remaining sampling period (July 2003) (Fig 4). The average SST decreased over the sampling period with intra-annual fluctuations. There were higher temperatures during spring and fall (Northern Hemisphere) with an average of ~30.0°C. Lower temperatures are recorded during winter and summer with an average of ~27.5°C. The DI-$\delta^{13}C$ increased independent of seasonal variation in SST. However on seasonal timescales, DI-$\delta^{13}C$ and Chlorophyll *a* were coupled such that when Chlorophyll *a* values increased drastically, DI-$\delta^{13}C$ values decreased.

Saipan DI-$\delta^{13}C$

The DI-$\delta^{13}C$ gradually increased over the entire record with more drastic fluctuations in $\delta^{13}C$ from October 2001 to August 2002, followed by a steady increase in $\delta^{13}C$ during the rest of the sampling period (Fig 5). The SST in Saipan had a pronounced seasonal cycle with lower temperatures in March (averaging 27.4°C) and higher temperatures in September (averaging 29.5°C). The Chlorophyll *a* data from Saipan shows very little fluctuation in concentration over the studied period (0.050 ±0.009 mg m^{-3}). The DI-$\delta^{13}C$ increased independent of SST and Chlorophyll *a*.

Hawai'i DI-$\delta^{13}C$

The DI-$\delta^{13}C$ in Hawai'i ranged between -0.78‰ and 1.06‰ (Fig 6). The period between March 1, 2003 and April 19, 2003 showed the most drastic fluctuations in DI-$\delta^{13}C$ and the period between April 26, 2003 and May 18, 2004 displayed more subtle fluctuations in DI-$\delta^{13}C$. The SST and Chlorophyll *a* data lack inner-annual to annual variations within the given time frame. The DI-$\delta^{13}C$ values in vary independently of SST and Chlorophyll *a* during the study period (March 1, 2003 to May 18, 2004).

DISCUSSION

Panama

Upwelling events bring deep, cool, nutrient rich water to the surface, stimulating biological processes such as primary production (i.e., Chlorophyll *a*) (Fig. 3). Upwelling drives the DI-$\delta^{13}C$ fluctuation in Panama from February to May of 2003 as indicated by the coupling of the DI-$\delta^{13}C$ and the SST. The depletion of DI-$\delta^{13}C$ after the upwelling event ceases is most likely due to respiration of detrital material as nutrients are used up. This is further supported by the minimal Chlorophyll *a* value post upwelling. Supplemental time series concentrations of DOC and POC could help to make the statement conclusive if the values decreased. Decreased concentrations of DOC and POC during the DIC sampling period would indicate that organic carbon was being converted into inorganic carbon.

Palau and Saipan

In Palau, an increase in Chlorophyll *a* density indicated an increase in primary production suggesting that nutrient rich and $\delta^{13}C$ depleted DIC water masses were migrating into the region through horizontal advection (Fig. 4). The lack of any relationship between SST, Chlorophyll *a*, and DI-$\delta^{13}C$ in Saipan make it difficult to determine which factors were driving DI-$\delta^{13}C$ variability (Fig. 5). However, given Saipan's proximity to Palau and the similar DI-$\delta^{13}C$ trends for each location, we propose that variation in regional mixing of surface currents must drive DI-$\delta^{13}C$ in Saipan and Palau. Palau and Saipan's differing SST annual variations dampen the argument for their regional association. A better understanding of seasonal and annual current models could be helpful in understanding the relationship between the two locations if they are in the same regional setting we propose.

Hawai'i

The independent variation of DI-$\delta^{13}C$ in relation to the SST and Chlorophyll *a* data makes it difficult to relate open ocean processes such as water mass mixing as the driving force of DI-$\delta^{13}C$ fluctuations. The location of the sampling site may also serve as a buffer for open ocean processes. In this barrier reef protected bay, we propose that coastal processes, such as river runoff may play more of a role in DI-$\delta^{13}C$ than open ocean surface seawater mass movements and ocean-atmosphere interactions. Rainfall events flush soil and other particulates from terrestrial environments out to sea via river catchment systems affecting the $\delta^{13}C$ values in seawater (i.e. Amazon River) [(Raymond, Bauer 2001; Druffel et al. 2005)]. Further examination of the rainfall and flooding patterns in the bay may shed light on the DI-$\delta^{13}C$ variation at this site.

All sites

Overall, these data demonstrate the influence of surface currents and water mass mixing (Panama, Palau, and Saipan), as well as coastal influences (Hawai'i) on seawater DI-$\delta^{13}C$ values. Use of DI-$\delta^{13}C$ based equations developed by (Quay et al. 1992) could be used to expand the current number of locations for which we have the spatial variability in oceanic uptake of atmospheric CO_2 over time. Such calculations are critical to fine-tuning our understanding of the role of the oceans in the global carbon cycle.

ACKNOWLEDGEMENTS

Field and Laboratory assistance: R. Moyer, Y. Matsui, J. Kloulechad, D. Idip, P. Colin, T. Isamu, J. Bauer, J. Moots, S. Takahashi, D. Purcell, R. Richmond, P. Jokiel, M. Lesser, T. Pease, P. Petraitis, O. Gibb, M. Cathey, L. Bloch, S. Higa, C. Smith, J. Philippoff, A. Larkum, L D'Croz, Palau International Coral Reef Center, Coral Reef Research Foundation, Palau Division of Marine Resources, Palau Ministry of Resources & Development, Commonwealth of the Northern Mariana Islands (CNMI) Division of Fish and Wildlife, CNMI Department of Environmental Quality, CNMI Coastal Resources Management, the University of Guam, University of Pennsylvania, Hawaii Institute of Marine Biology, Department of Land and Natural Resources Hawaii, and the Smithsonian Tropical Research Institute, and NASA's Goddard Earth Sciences Data and Information Services Center Giovanni project. Research funding provided by grants from American Society for Mass Spectrometry, the Mellon Foundation, University of Pennsylvania Research Foundation, Woodrow Wilson National Career Enhancement Fellowship for Junior Faculty, the Petroleum Research Foundation (grant #41740-G), and the National Science Foundation programs in Chemical Oceanography (OCE#0426022) and Biological Oceanography (OCE#0542415).

FIGURE LEGENDS

Fig. 1 Map of the Central Pacific Ocean showing the sample collection sites of Panama, Palau, Hawai'i and Saipan along with the three major water currents in the region.

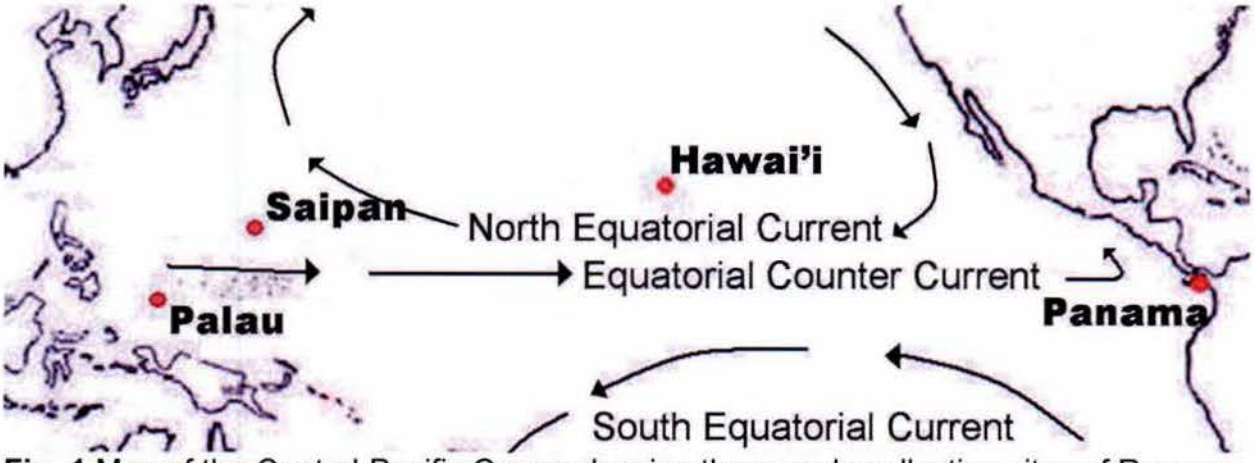
Fig. 2 Weekly DI-$\delta^{13}C$ values from Panama, Saipan, Palau, and Hawai'i from 2001- 2004.

Fig. 3 DI-$\delta^{13}C$ in Panama was coupled with the sea surface temperature (SST) and chlorophyll during upwelling [Feb to May] and decoupled post-upwelling. . Dashed line indicates the end of the upwelling period.

Fig. 4 DI-$\delta^{13}C$ values in Palau decreased as Chlorophyll *a* increased, independent of sea surface temperature (SST).

Fig. 5 DI-$\delta^{13}C$ values in Saipan varied independently of sea surface temperature (SST) and Chlorophyll *a*.

Fig. 6 DI-$\delta^{13}C$ values in Hawai'i fluctuated independently of sea surface temperature (SST) and Chlorophyll *a*.



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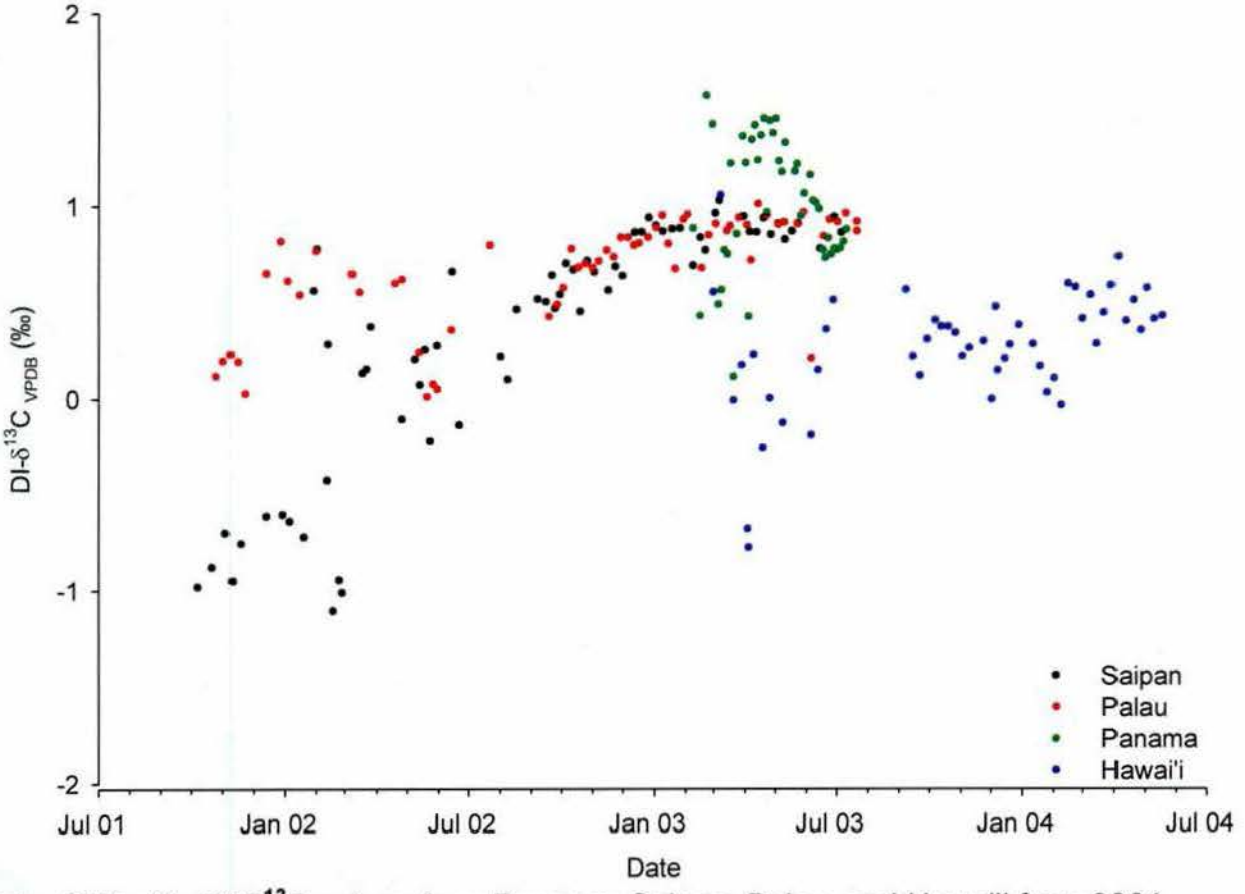

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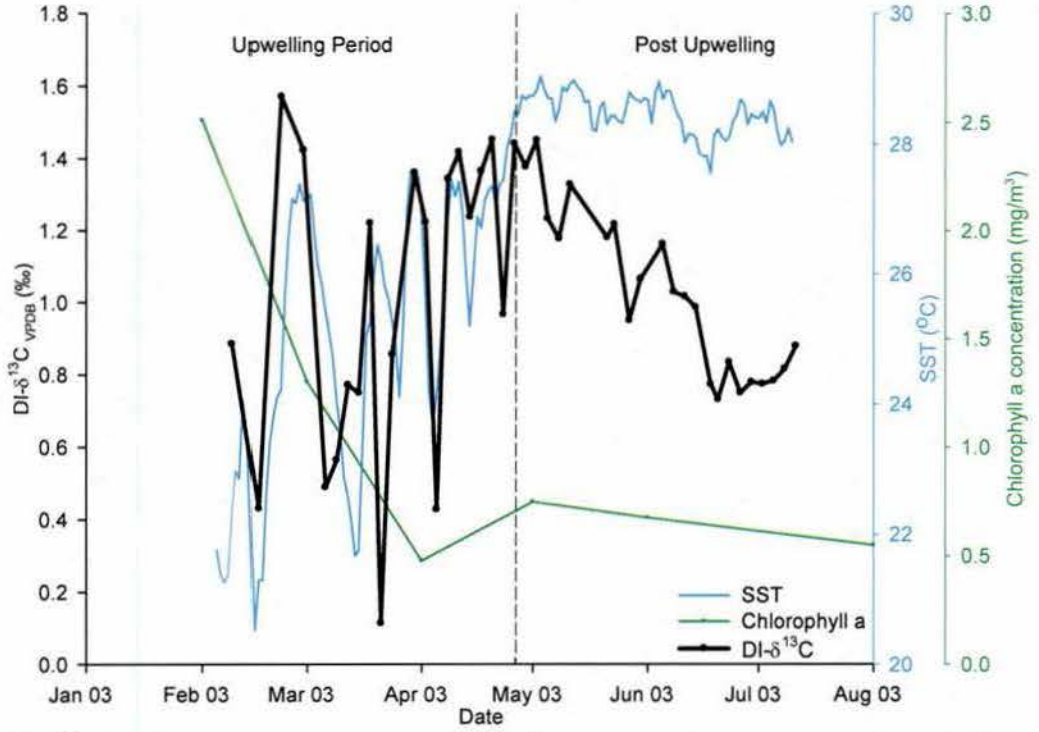

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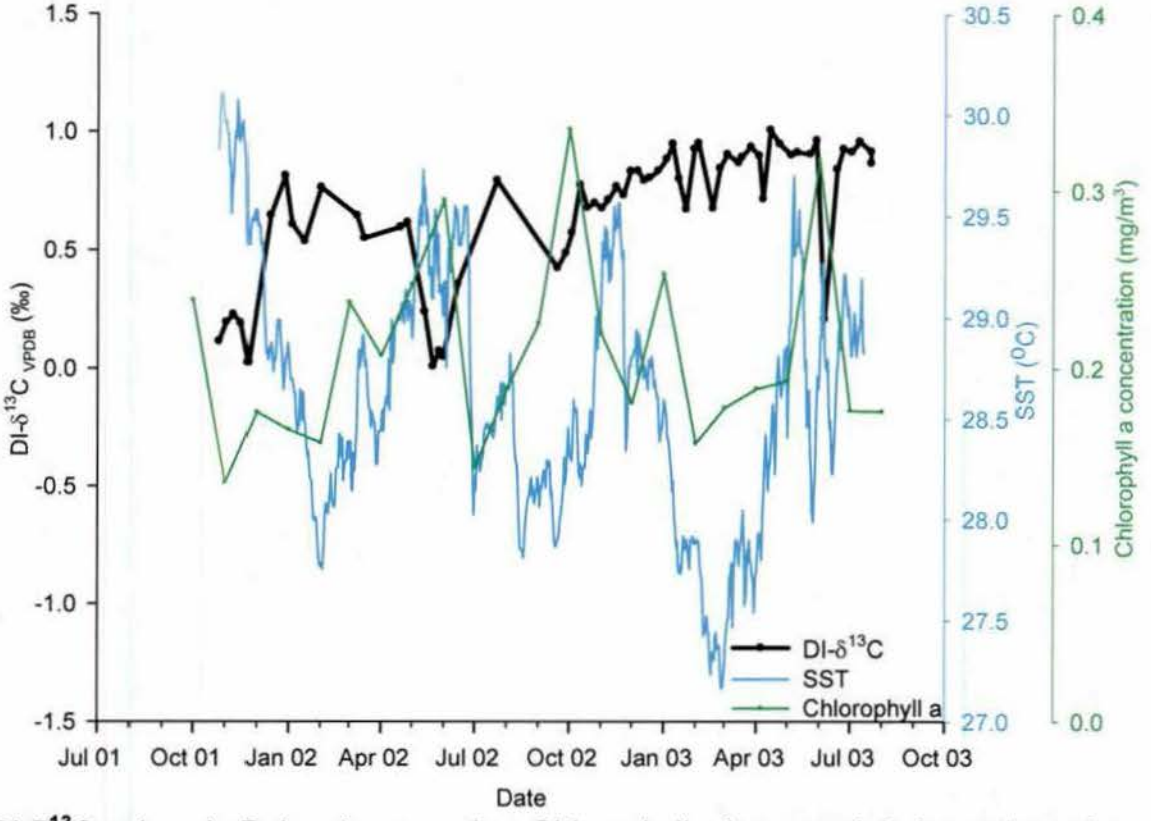

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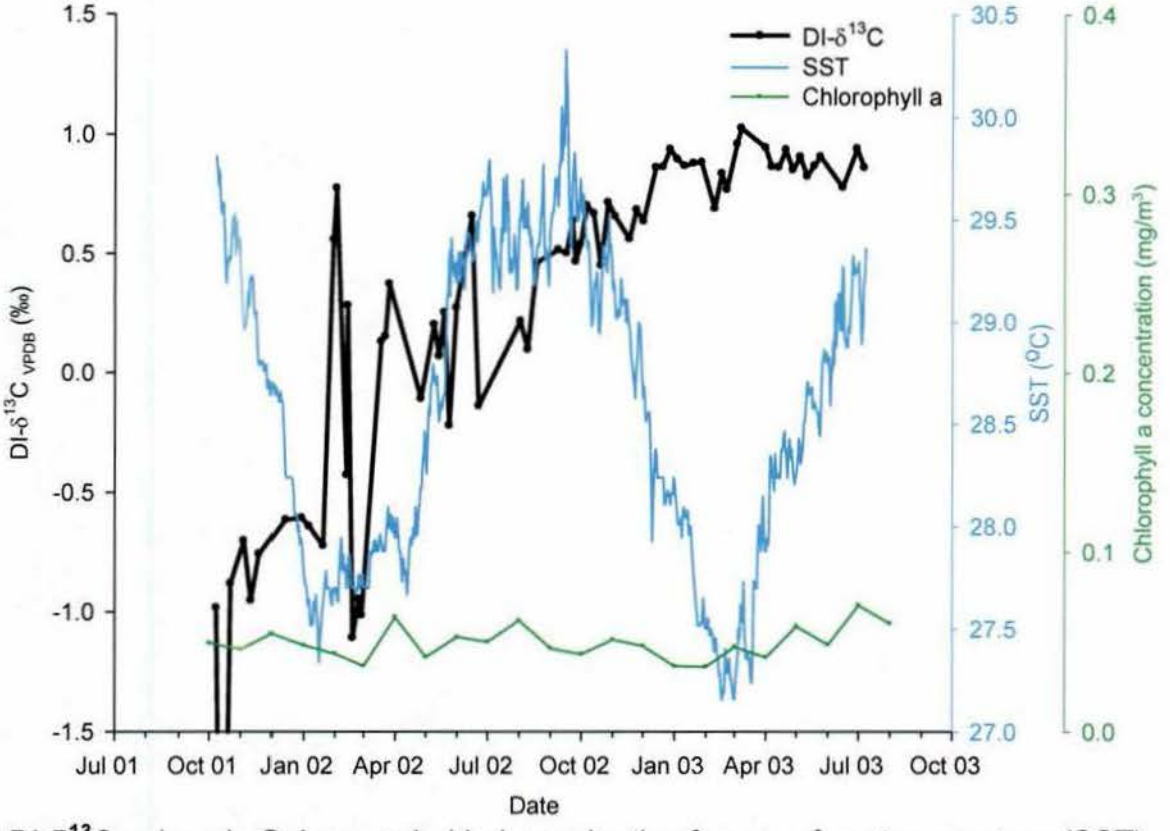

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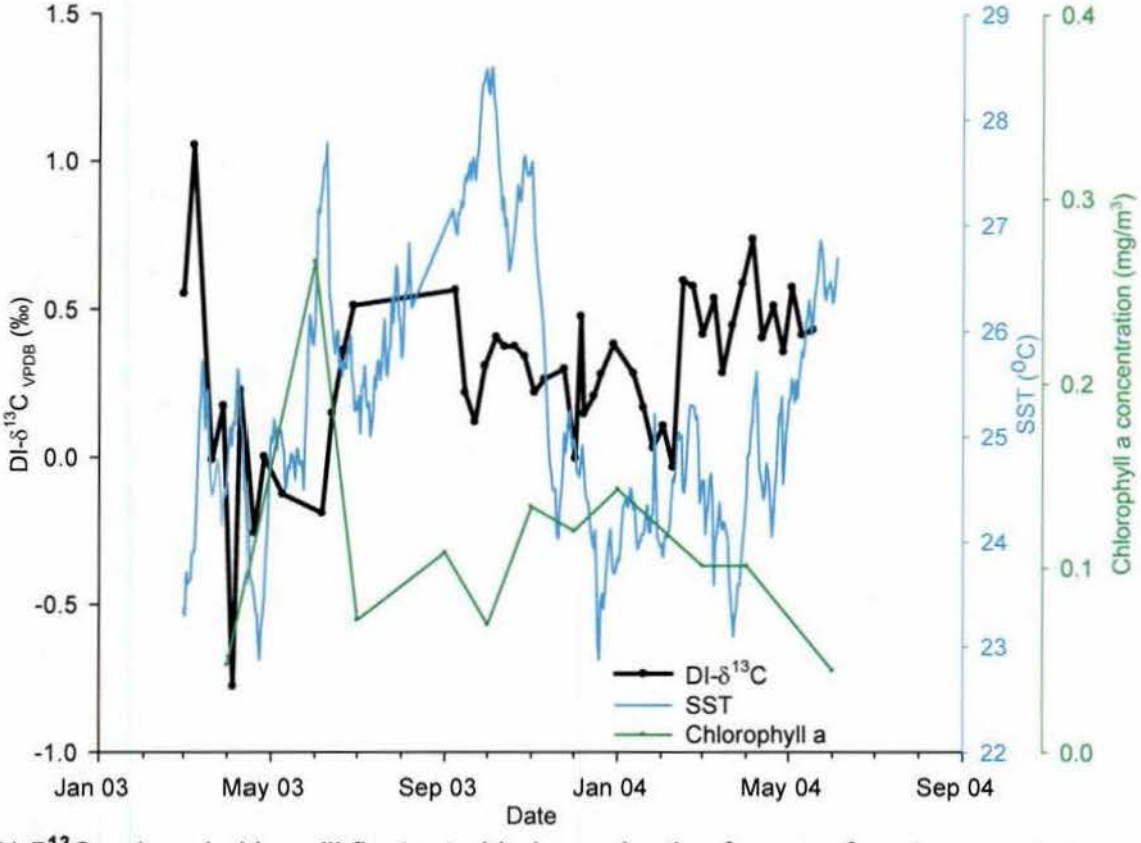

Fig. 6 DI-$\delta^{13}C$ values in Hawai'i fluctuated independently of sea surface temperature (SST) and Chlorophyll *a*.

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